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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

1 June 1994 through 31 May 1995

OFFICE OF NAVAL RESEARCH

GRANT N00014-90 J-1263

R&T PROJECT 4133002—12

SOLVATION DYNAMICS AND THE STRUCTURE IN ELECTROLYTES AND ELECTRODES

PRINCIPAL INVESTIGATOR

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R&T Number: 4133002—12

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Grant Title: SOLVATION DYNAMICS AND THE STRUCTURE IN ELECTROLYTES AND ELECTRODES

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- a. Number of papers submitted to refereed Journals, but not published: 8
 - b. Number of papers published in refereed Journals (list attached): 5
 - c. Number of books or chapters submitted, but not published: 2
 - d. Number of books or chapters published (list attached): 0
 - e. Number of printed technical reports & non refereed papers (list attached): 0
 - f. Number of patents filed: 0
 - g. Number of patents granted: 0
 - h. Number of invited presentations at workshops or professional society meetings : 11
 - i. Number of presentations at workshops or professional society meetings : 8
 - j. Honors/Awards/Prizes for contract /grant employees (list attached): 5
 - k. Total number of graduate students and post-doctoral associates supported at least 25% during this period:
 - Graduate students: 2
 - Post-Doctoral associates: 2
- including the number of,
- Female graduate students: 0
 - Female Post-Doctoral associates: 0
- the number of,
- Minority Graduate Students: 1
 - Minority Post-Doctoral associates: 2
- and the number of,
- Asian Graduate Students: 0

Asian Post-Doctoral associates: 0

I. Other funding:

1. NSF-Epscor

Materials Science Research Center

\$50,000.- (1992-1994) Under no-cost extension

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PART I

a. Papers Submitted

1. M. Legault, L. Blum and D. A. Huckaby, A MEAN FIELD TREATMENT OF THE HARD HEXAGON INTERACTIONS IN THE HB MODEL, 2nd Ulmer Elektrochemische Tagung (1995).
2. D. A. Huckaby and L. Blum, A MODEL FOR THE UNDERPOTENTIAL DEPOSITION OF METALS, in *Diffusion Processes: Experiment, Theory, Simulations*, A. Pekalski, Editor, Springer Verlag, Berlin (1994).
3. O. Pizio and L. Blum, ANALYTIC SOLUTION OF THE MEAN SPHERICAL APPROXIMATION FOR A DIPOLAR HARD SPHERE FLUID WITH INTRACORE ANISOTROPIC STICKY INTERACTIONS, Phys. Revs. E., (19).
4. L. Blum and F. Vericat AN ANALYTICAL MODEL OF WATER WITH STICKY SPHERES OF TETRAHEDRAL SYMMETRY Mol. Phys. (19), issue commemorating the 60th birthday of Douglas Henderson.
5. L. Blum and F. Vericat, WATER AS HARD-SPHERES WITH A STICKY POTENTIAL OF TETRAHEDRAL SYMMETRY J. Phys. Chem., (19).
6. A. Chhah, P. Turq, O. Bernard, J. M. G. Barthel and L. Blum, TRANSPORT COEFFICIENTS AND APPARENT CHARGES IN CONCENTRATED ELECTROLYTE SOLUTIONS: EQUATIONS FOR PRACTICAL USE, Ber. Bunsenges, (1994).
7. L. Blum and O. Bernard, THE GENERAL SOLUTION OF THE ASSOCIATING MEAN SPHERICAL APPROXIMATION FOR DIMERIZING IONS, J. Statistical Phys.,
8. L. Blum and Léo Degève, MONTE CARLO STUDY OF ANALYTIC POTENTIALS FOR WATER, J. Phys. Chem., (19).

b. Papers Published in Refereed Journals

1. L. Blum, M. Legault and P. Turq, KINETIC THEORY FOR ELECTRODIC PHASE TRANSITIONS: THE VOLTAMMOGRAM J. Electroanal. Chem. 379 35 (1994).
2. L. Blum, CONTACT THEOREMS FOR ROUGH INTERFACES, J. Stat. Phys., 75 971 (1994).

3. L. Blum and D. A. Huckaby, UNDERPOTENTIAL DEPOSITION OF Cu ON Au(111): IMPLICATIONS OF THE HB MODEL, J. Electroanal. Chem. 375 69 (1994).
4. Dongqing Wei and L. Blum, THE SOLVATION THERMODYNAMIC FUNCTIONS IN THE MEAN SPHERICAL APPROXIMATION (MSA): BEHAVIOR NEAR THE SOLVENT CRITICAL REGION, J. Chem. Phys., 102 4217 (1995).
5. L. Blum, F. Vericat and D. Bratko, TOWARDS AN ANALYTICAL MODEL OF WATER: THE OCTUPOLAR MODEL, J. Chem. Phys., 102 1461 (1995).

c. Books in Print

1. *Electrolytes at Interfaces.*

P. Turq, J.P. Simonin and L. Blum,
Kluwer, Amsterdam, (In preparation, 1991).

2. J. R. Grigera, L. Blum and E.H. Stanley, Biophysics of Water (Springer Verlag)

d. Books Published

None

e. Technical Reports

1. O. Pizio and L. Blum, ANALYTIC SOLUTION OF THE MEAN SPHERICAL APPROXIMATION FOR A DIPOLAR HARD SPHERE FLUID WITH INTRACORE ANISOTROPIC STICKY INTERACTIONS, Phys. Revs. E. , (19).
2. L. Blum and F. Vericat AN ANALYTICAL MODEL OF WATER WITH STICKY SPHERES OF TETRAHEDRAL SYMMETRY Mol. Phys. (19), issue commemorating the 60th birthday of Douglas Henderson.
3. L. Blum and F. Vericat, WATER AS HARD-SPHERES WITH A STICKY POTENTIAL OF TETRAHEDRAL SYMMETRY J. Phys. Chem., (19). Harold Friedmann Festschrift.
4. L. Blum and O. Bernard, THE GENERAL SOLUTION OF THE ASSOCIATING MEAN SPHERICAL APPROXIMATION FOR DIMERIZING IONS, J. Statistical Phys.,
5. M. Legault, L. Blum and D. A. Huckaby, A MEAN FIELD TREATMENT OF THE HARD HEXAGON INTERACTIONS IN THE HB MODEL, 2nd Ulmer Elektrochemische Tagung (1995).

6. D. A. Huckaby and L. Blum, A MODEL FOR THE UNDERPOTENTIAL DEPOSITION OF METALS, in *Diffusion Processes: Experiment, Theory, Simulations*, A. Pekalski, Editor, Springer Verlag, Berlin (1994).
7. L. Blum and F. Vericat AN ANALYTICAL MODEL OF WATER WITH STICKY SPHERES OF TETRAHEDRAL SYMMETRY *Mol. Phys.* (19), issue commemorating the 60th birthday of Douglas Henderson.
8. A. Chhah, P. Turq, O. Bernard, J. M. G. Barthel and L. Blum, TRANSPORT COEFFICIENTS AND APPARENT CHARGES IN CONCENTRATED ELECTROLYTE SOLUTIONS: EQUATIONS FOR PRACTICAL USE, *Ber. Bunsenges*, (1994).

f. Patents filed:

None.

h. Invited Conferences

1. FOURTH LIBLICE CONFERENCE ON THE STATISTICAL MECHANICS OF LIQUIDS, Liblice, Czech Republic, June 6-10, STRUCTURED CHARGED INTERFACES: THEORY AND EXPERIMENT. Plenary Lecture.
2. FOURTH LIBLICE CONFERENCE ON THE STATISTICAL MECHANICS OF LIQUIDS, Liblice, Czech Republic, June 6-10, THE SOLUTION OF THE ORNSTEIN ZERNIKE EQUATION FOR ANISOTROPIC STICKY SPHERES : TOWARDS AN ANALYTICAL MODEL OF WATER, Invited Lecture.
3. MODELIZATION OF UNDERPOTENTIAL DEPOSITION: THE Cu ON Au(111) INTERFACE, A Cecam workshop, Centre de Calcul Atomique et Moleculaire, Lyon, France, June 15-17, 1994, Organizer of the Workshop.
4. 2nd Ulm Symposium of Electrochemistry, June 20-21, 1994
A MEAN FIELD TREATMENT OF THE HARD HEXAGON INTERACTIONS IN THE HB MODEL

Invited Lecture.

5. SCALING CONCEPTS IN COMPLEX FLUIDS, Catanzaro, Italy, July 4-8, 1994 STICKY MODEL OF CHARGED COLLOIDS,
Oral presentation
6. ADVANCES IN THE MEASUREMENT AND MODELING OF SURFACE PHENOMENA, 400th
Anniversary Symposium, San Luis, Argentina, 24-30 August, 1994.
PHASE TRANSITIONS AT THE CRYSTAL SOLUTION INTERFACE.
Invited Lecture.
7. IUVESTA Workshop, SURFACE SCIENCE AND ELECTROCHEMISTRY, San Benedetto del Tronto, 12-16 September 1994,
STRUCTURE AND KINETICS OF THE UPD OF Cu ONTO Au(111).
Invited lecture.
8. Symposium in Honor of Douglas Henderson's 60th Birthday,
STATISTICAL MECHANICS OF FLUIDS, Mexico 3-4 October 1994,
ANALYTICAL MODEL OF LIQUID WATER,
Plenary speaker.
9. STRUCTURE, ENERGETICS, AND DYNAMICS IN THE LIQUID PHASE,
Symposium in Honor of Harold Friedmann, State University of NY at Stony Brook, March 25, 1995,
ANALYTICAL MODEL OF LIQUID WATER,
Plenary speaker.
10. COLLOID AND INTERFACE SCIENCE: TRENDS AND APPLICATIONS,
Workshop to be held in Copamarina Beach Resort,
Guanica, Puerto Rico, May 3-5, 1995
Organizers: Lesser Blum (U. of Puerto Rico) and Sow-Hsin Chen (MIT)
11. Snowdonia Conference on the Dynamics and Structure
at Electrified Interfaces, Harlech, England July 17-21, 1995.

Member of International Advisory Committee.

Invited Speaker.

Topical Conferences

1. University of California, Berkeley, May 26, 1994 ANALYTICAL THEORY OF WATER
2. University of California, Davis, June 1, SCALING AND THE MEAN SPHERICAL APPROXIMATION.
3. IBM, Almaden Valley, June 3, 1994. ANALYTICAL THEORY OF WATER
4. Universite de Paris, Electrochimie, July 13 1994, RECENT RESULTS FOR THE UNDERPOTENTIAL DEPOSITION OF Cu ON Au(111).
5. University of Venice, Physics , Sept. 17, 1994, MEAN SPHERICAL APPROXIMATION AND SCALING : THE SOLUTION OF THE WERTHEIM CASE.
6. Universidad Nacional Autonoma de Mexico, Institute for Chemistry, Sept. 28, 1994, PHASE TRANSITIONS AT ELECTRODES: Cu/Au(111) UPD AS THE EXAMPLE.
7. Universidad de Puebla, Sept. 30, 1994 BIOPHYSICS OF WATER
8. University of Illinois, Urbana, Chemistry, November 11, 1994, UNDERPOTENTIAL DEPOSITION: THE Cu ON Au(111) SYSTEM.

j. Honors/Awards/Prizes

1. L. Blum, SPA, Scientific Productivity Award by the University of Puerto Rico, 1993.
2. Member, International Advisory Committee, Snowdonia Conference on Electrified Interfaces
3. Member, Editorial Committee of Physica (A) from 1996, for 3 years.
4. Organizer, CECAM Workshop on Underpotential Deposition, Lyon, France,
5. Organizer, COPAMARINA Conference on Colloid and Interface Science

PART II

a. Principal Investigator

Lesser BLUM

b. Current Telephone Numbers

Lesser Blum (809) 763-3390

c. Cognizant Scientific Officer

Robert J. Nowak

d. Description of Project.

We demonstrated in previous periods of this project, the techniques of EXAFS and X-ray scattering to study the in situ structure of metal and ionic adsorbates on single crystal electrodes. Amongst the tools for the in situ analysis of the electrode interface structure, we should mention the STM and AFM which are certainly some of the most popular techniques.

Each of these techniques provides data which has to be complemented by the others, and the full understanding of what is happening at the electrode needs models which have to be consistent with all available experimental evidence. This is not always the case, since on many occasions, apparent discrepancies arise.

We have studied the case of the underpotential deposition (UPD) of copper on gold (111) in the presence of sulphuric acid. We have developed a theory that explains the voltammogram in terms of structures that were found experimentally, and removed inconsistencies between different experimental groups.

The UPD of Cu onto Au(111) in the presence of bisulfate ions displays two peaks in the voltammogram. In our theory the role of bisulfate ion in this deposition process is the reversible formation of a honeycomb pattern, a fact that is confirmed experimentally.

We provided a theory for the zero speed scanning rate (equilibrium) voltammogram, that is easily adapted to the kinetic regime, yielding formulas for the shifts of the peaks for small scanning rates. In our work we discussed the kinetic constants of the UPD process, and how they are related to the shifts of the peaks of the voltammogram, the relation of the apparent and real charge of the adsorbate to the concentration shifts and to the surface compressibility of the adlayer.

More recently, we introduced modifications of the model to account for the finer details of the broad foot region of the voltammogram, the adsorption isotherm and of the quartz crystal microbalance curve. This is done introducing long range interactions between the sulfate ions adsorbed on the gold surface using an extension of the so-called Widom theorem, which allows for the introduction of both attractive and repulsive interactions between the adsorbed sulfate

ions. We get excellent agreement for both the voltammogram and the microbalance experiments.

Our fruitful collaboration with W.R.Fawcett on the question of electron transfer kinetics in bulk and electrode surface will be pursued. This is an issue of importance in the Marcus theory of electron transfer. Our basic approach is to use analytically solved models for the solvent, water, which can be also solved analytically for ionic solutions, both in the bulk and at interfaces. We will study both the structural and kinetic aspects of this work: the high frequency limit in which the polarizability dominates, by extending the successful Wei-Patey interpolating formalism for the van Hove functions in this limit. The high frequency limits will be studied using the newly developed theory of the quenched-annealed fluids, where the dipoles are quenched and the polarizability is annealed. The simple polarizable dipole hard sphere model developed earlier will be used, with the inclusion of a coupling mechanism to the tetrahedral hydrogen bond network of water. This can be done using a simple water intermolecular potential, consisting of hard spheres with a point dipole and an attractive potential well with the symmetry of a tetrahedral octupole was proposed sometime ago by Bratko, Blum and Luzar. This potential is solved analytically, and has been shown to agree very well with the structures determined by neutron diffraction.

e. Results

During 1990-1993, we proposed and developed a theory of the structural changes occurring in the UPD of Cu/Au(111) in the presence of sulfate (or bisulfate) ions. While initially not very well accepted, it has turned out to successfully predict the structure and transformations occurring during the deposition.

Although initially the STM indicated 5 by 5 structures for the copper adlayer after the second peak, later work showed that this was due to Cl impurities, and that the $\sqrt{3} \times \sqrt{3}$ predicted by our work is correct. The coverage controversy with the STM (which sees 1/3 coverage) was also clarified by recent experiments by Lipcowski, who confirms the 2/3 of our theory. Discrepancies within the foot region of the first spike are lifted by our most recent theory.

We have also developed a kinetic theory for slow scanning voltammograms, with which we will study the kinetics of UPD phase transformations.

Discreetness of solvent effects in electron transfer kinetics were investigated for a number of nonaqueous solvents in the homogeneous bulk mode. Very encouraging correlations between the activation parameters were found for large sets of solvents.

The new analytical explicit solution of the sticky tetrahedral water model will permit extensions of the dipole model to realistic situations. This model compares surprisingly well with the best structure of liquid water from neutrons as obtained by Soper and Silver. We hope to be able to obtain simple relations between the structure forming parameters of Blum and Fawcett and the tetrahedral hydrogen bonding parameters of the recent work of Blum and Vericat. The dynamic and chemical association effects have been studied with simple models (MSA), and excellent agreement to experiment.

f. Summary of Plans

Phase transitions occurring during electrode processes have been studied using a model in which the electrode is a planar wall with sticky adsorption sites. This model was used to explain the underpotential deposition (UPD) of copper on gold (111) in the presence of bisulfate ions. The model assumes that the bisulfate ions form a template for the adsorption of the first 2/3 of a monolayer of copper onto a honeycomb lattice. The centers of the hexagons that form the honeycomb are occupied by the bisulfate. In the absence of copper the bisulfate is desorbed as the electrode becomes more negatively charged, and for that reason the template 'melts' when the fraction of occupied sites drops below a certain critical value, which is estimated using the hard hexagon model of Baxter. We assume strong copper-bisulfate coadsorption, so that in the presence of a sufficiently large amount of Cu the template is reconstructed. Our model explains the qualitative features of the voltammogram, and makes definite predictions for the structures that should be observed. In previous work, we separated the problem as a second order phase transitions for the bisulfate, and a sequence of two first order phase transitions for the copper. The coupling of the copper and the bisulfate was treated in a simple mean field approximation. In the present work we go a step beyond this simple model: We introduce a model with individual couplings (copper-copper and copper-bisulphate), and use the method of cluster variation to solve approximately the complicated lattice problem in which the bisulphate excludes the first neighbors and the copper is always attractive. An approximate theory is constructed using the cluster variation method of Guggenheim and McGlashan.

We plan to pursue the studies on the structure and dynamics of the phase transformations at electrode interfaces and the solvation dynamics and structure in relation to the Marcus theory.*

- We will develop a detailed theory for the underpotential deposition (UPD) of Cu/Au(111) in the presence of selected anions, in terms of ion-metal and ion-ion interactions. The two major ingredients are a modified Guggenheim and McGlashan cluster variation method, and an extension of the Baxter hard hexagon model to attractive and repulsive hexagons using the Widom theorem. Potential shifts and kinetic aspects pertaining to the film formation will be studied. This will be applied to other cases, such as Cu/Pt(111), in which the voltammogram shows one spike for low sulfuric acid concentrations, and two for high concentrations, and to other cases which involve even more complicated interactions. The immediate goal is to define lateral and adsorption interaction parameters, with which we can predict the sequence of phase formation. The long range idea is to establish empirical rules (somehow reminiscent to the Woodward-Hoffman rules) for the formation of ordered structures on metal surfaces.

- develop a kinetic and equilibrium theory for the bisulphate adsorption, which includes the extension of our kinetic theory to the multicomponent case.
- Study of the consequences of the model in relation to chronocoulometry, microbalance, adsorption using Esin Markov equations.
- Study the voltammogram shifts of the peaks, in their relation to the overall kinetic reaction constants.
- Study of the STM image theoretically. We will perform a theoretical calculation of the electronic structure of the honeycomb intermediate step of our problem, to explain the apparent contradiction in the STM result of Itaya, which yields 1/3 of copper coverage and our theory, which requires 2/3 of a Cu monolayer. This will be done in collaboration with Profs. L. Foseca and F. Zypman of our University and the Centre de Calcul of the University of Montreal.

In the problem of dynamics of solvation we plan to :

- Develop the quenched-annealed formalism to study the high frequency limit of a system of spheres with a permanent dipole moment and polarizability. This approach was never used when studying the optical dielectric limits of the solvation energies, an important parameter in Marcus theory.
- Use the new analytical explicit solution of the sticky tetrahedral water model to study the low frequency response of the dielectric constant and solvation energy. We will find simple relations between the structure forming parameters of Blum and Fawcett and the tetrahedral hydrogen bonding parameters of the recent work of Blum and Vericat.
- Use the microfield formulation developed some years ago to compute the van Hove response functions of a molecular solvent in the high and low frequency limits.

We will continue this work in the framework of the collaboration with Prof. R.W. Fawcett to study solvent effects in electrokinetics.

g. Graduate Students

1. Marc Legault (UPR)
2. Esob Velasquez (UPR)

h. Post-Doctoral

1. D.Q. Wei

2. F. Vericat

PART III

STRUCTURE AND TRANSFORMATIONS IN ELECTRODES

The structure and transformations of the copper monolayer UPD deposited onto gold (111) is discussed. We explain the role of the sulfate and its transformations and predict the structures by X-rays and STM. We show which interactions produce phase transformations, and correctly explain the voltammogram and adsorption isotherm.

(Figure 1)

'Marcus' adapted Water model

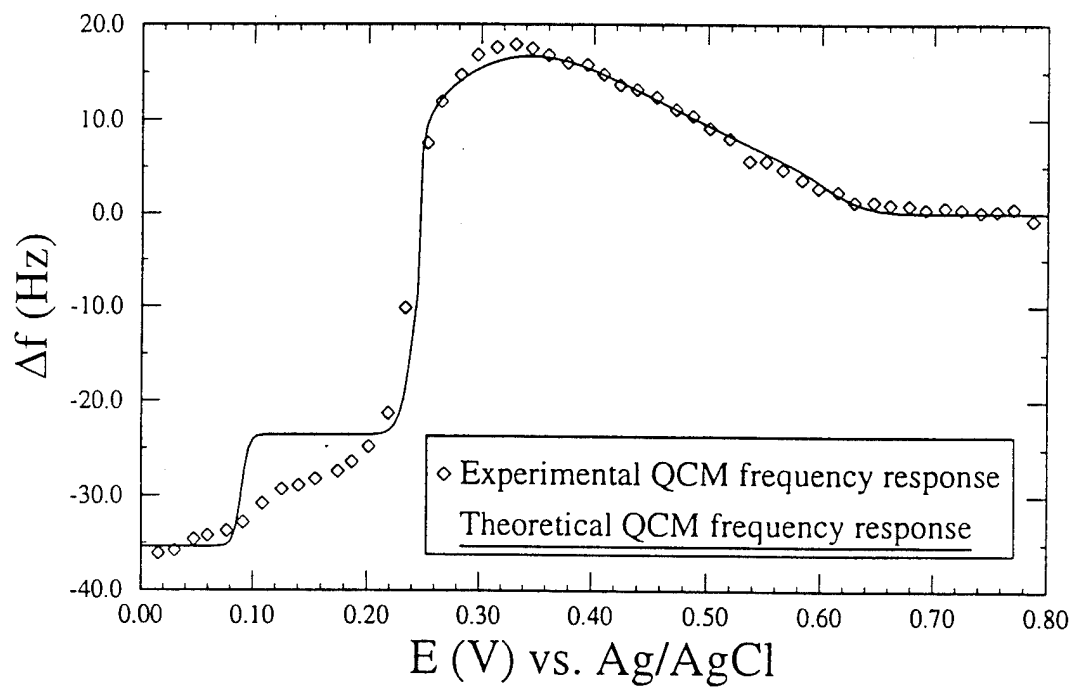
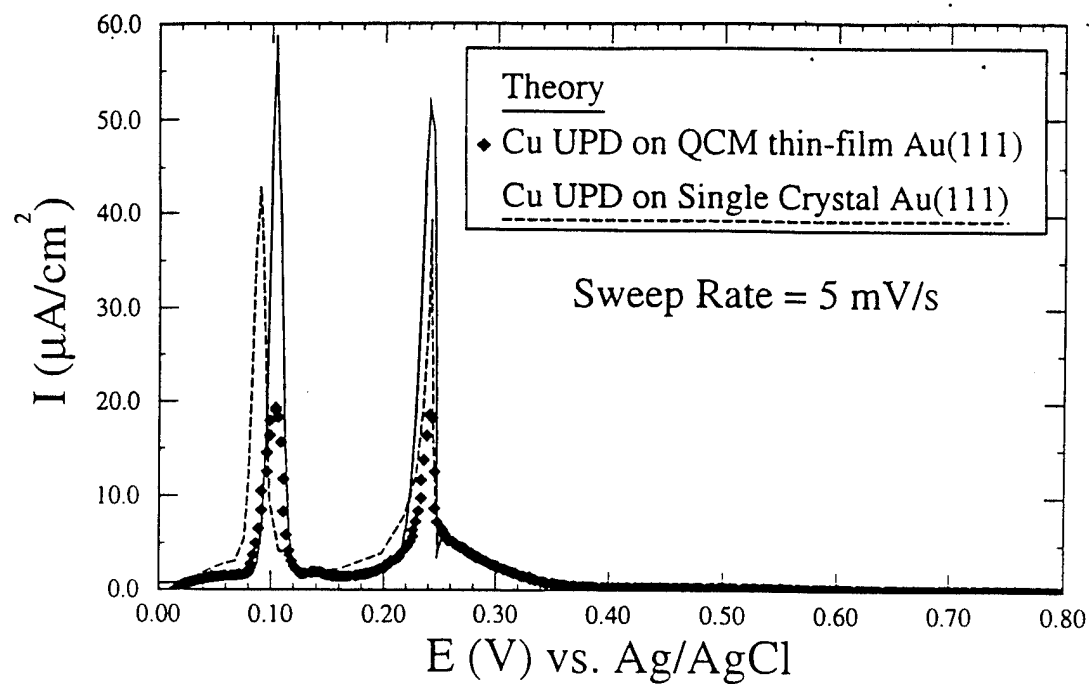
Develop an analytical model of water to be used in the molecular Marcus theory of electron transfer.

The model has a polarizable dipole and a tetrahedral potential to mimic hydrogen bonds. A new analytical solution has been found, and compared to the experimental neutron diffraction structure pair distribution functions is shown in figures 2,3,4

Theoretical Results:

- 1. Formulation of a kinetic theory for the underpotential deposition of Copper on Gold (111) in the presence of Sulphuric acid.**
- 2. Explicit analytical solution of a model of water that has correct structure and is simple enough for Marcus theory.**

Figure 1



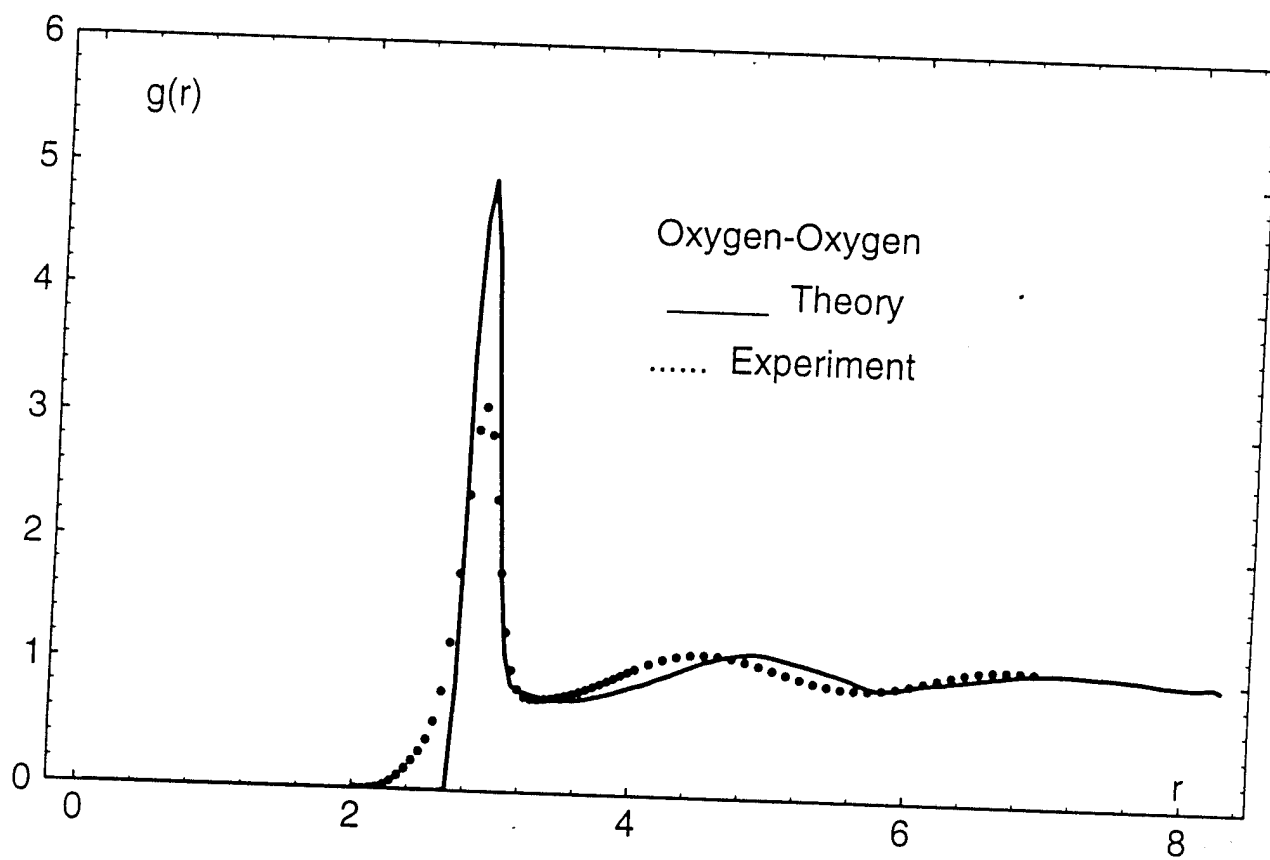


Figure 2

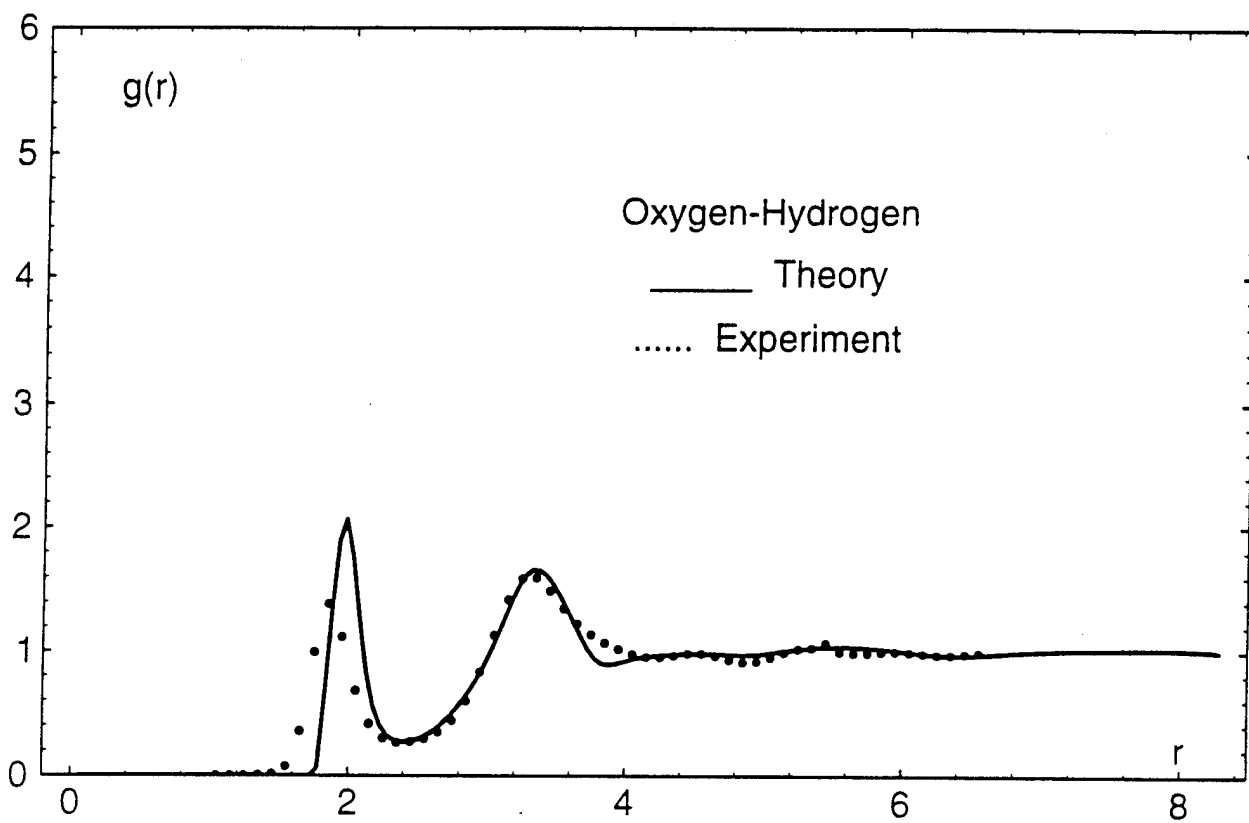


Figure 3

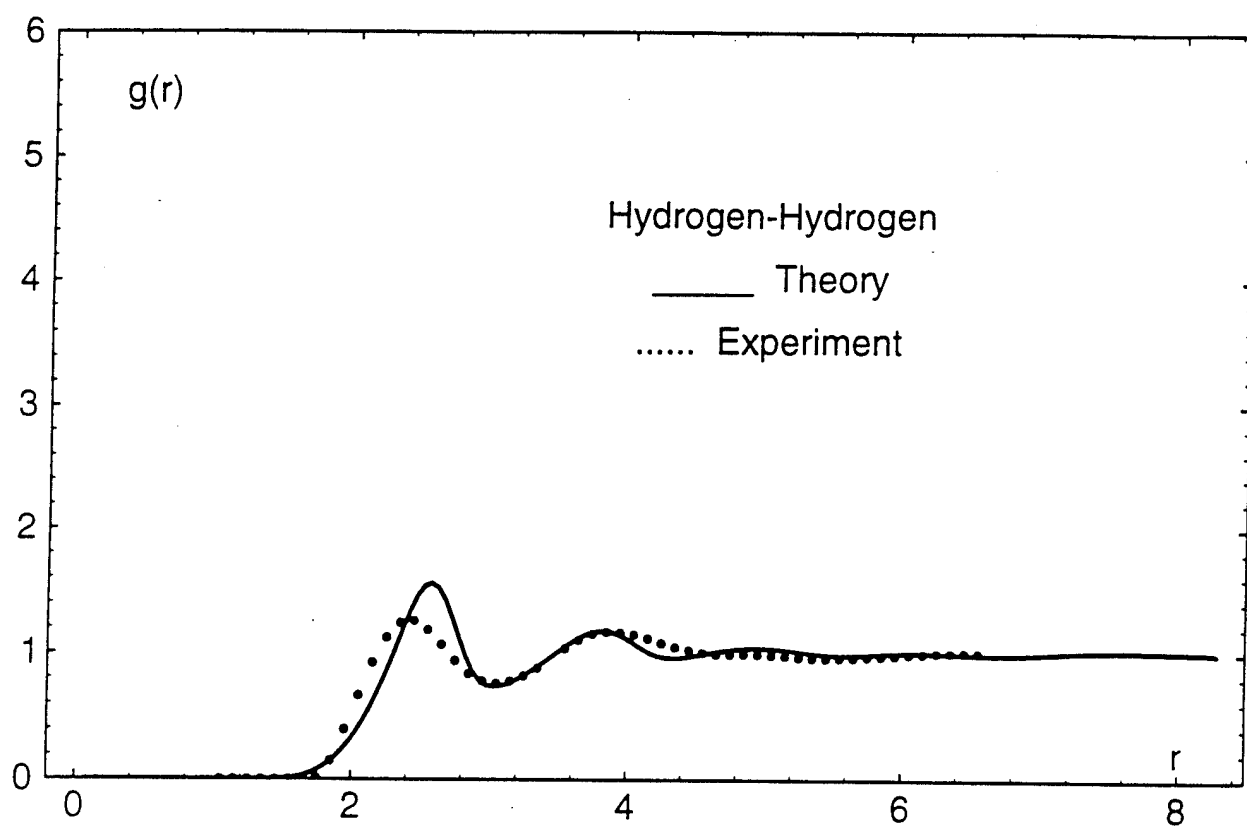


Figure 4